Periodical

SUPPLEMENT TO THE ENGINEER, DECEMBER 29, 1933.

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The Metallurgist.

Supplement to The Engineer, *December, 1933.*

High-Temperature Engineering.

SOME years have now elapsed since THE METALLURGIST was among the first to urge the necessity for more extensive and more systematic investigation of materials for use at high temperatures. It was realised at that time, and we pointed it out repeatedly, that for progress in the use of high temperatures, whether for the purpose of securing greater efficiency in our prime movers or for allowing the use of higher temperatures and pressures in some of our chemical operations, the development of new and better materials was essential, and that, in fact, the progress of engineering in these directions had become almost entirely a problem of materials. To-day this fact needs no urging since the trend towards the use of high temperatures has become more marked as time has progressed and working temperatures and pressures are employed to-day which were still regarded as beyond the limits of practical attainment some four or five years ago. This is the result, to some extent, of a better knowledge of the behaviour of materials at high temperatures which is one of the products of the very research which we advocate. It must, however, be confessed in part that our present-day practice is based upon the use of working stresses at high temperatures which would not have been admitted some years ago. There are, it is true, high-class materials available which possess remarkable properties at high temperatures, but many of them are too expensive to be widely used, and their employment is confined to special purposes where the quantities involved are not too large and the cost does not, therefore, become prohibitive.

Broadly speaking, however, it is clear to-day even more than it was five years ago that further advance of knowledge in regard to materials capable of bearing serious working stresses at high temperatures is urgently needed, together with all that knowledge of the general behaviour and properties of different metals and alloys, when used at high temperatures, which flows as a kind of by-product from the main research on such materials. Unfortunately, the actual state of research does not correspond adequately with this need. Excellent work has been done in a number of laboratories, notably at the National Physical Laboratory, and in the works of some of our most progressive steel makers and manufacturers, but it has not been done, in our opinion, on an adequately large scale, so that progress has not been as rapid as it should.

Roughly speaking, the subject divides itself into two groups. The first and perhaps the more humble group relates to steels which, from cheapness and ease of manufacture, can be used in large quantities for such purposes as steam boilers, superheater tubes and similar apparatus required in high-temperature steam engineering, and in some portions also of internal combustion motors. In this class of materials the limit of price would appear to prohibit the use in any large quantity of alloying elements, and also the use of materials whose strength and hardness at high temperatures would make it difficult, if not impossible, to shape them by the ordinary methods of forging and rolling. On the other hand, the upper limit of temperature as yet envisaged for materials of this kind probably lies in the neighbourhood of 400 deg. or at most 500 deg. Cent. The second group relates to materials intended for use at considerably higher temperatures, ranging up to 800 deg. or even 1000 deg. Cent. Here the question of expense cannot be considered in the same manner, while obviously if a material is to be capable of bearing a serious working stress for a prolonged period at 800 deg. or 1000 deg. Cent., we cannot hope to be able to shape it by rolling and forging at that temperature or by the methods generally employed. At the same time the sphere of application of materials of this kind is much more limited. Certain parts of internal combustion engines, such as exhaust valves and their seatings, are exposed to these very high temperatures, while the runners of exhaust turbines and ultimately the rotors of internal combustion turbines must also withstand heat at least of this order. As yet such parts are only small, and it may be sufficient to be able to produce them in the cast state with the aid of some of the more expensive alloying metals and possibly with the exclusion of iron as an important constituent. In this direction also important progress has been made.

A third series of difficulties arises in regard to the determination of the properties of such high-temperature materials. Research has given us the conception of "creep," and we have come to realise that short-time tensile tests at high temperatures in themselves are of little value. Unfortunately, the standard methods of determining resistance to creep are very lengthy and the engineer is inclined to regard them as unpractical from his point of view. While his need for a "short cut" can be readily understood, the scientific metallurgist must, unfortunately, impose a veto upon tests which, while apparently giving satisfactory results, may yet give rise to misleading conclusions. The phenomena of failure at high temperatures are very different from those of fracture at room temperature. We need mention only intercrystalline separation which may occur with or without appreciable previous flow or extension.

All these matters have been receiving attention to a certain extent under the auspices of two Research Committees. One of these, which is a Committee of the Department of Scientific and Industrial Research, and is generally known as the "Main Committee" on Materials at High Temperatures, deals, within the

limits of its financial resources, with materials of the second group to which we have referred above, and with certain fundamental questions relating to the behaviour of metals at high temperatures. The first group of materials (steels) are the care of another Committee, which is a joint body of the Department of Scientific and Industrial Research and the Electrical Research Association, the latter being very much interested in the question on behalf of the builders of turbine plant. This second or Joint Committee is nominally a Sub-committee of the first, but in reality, we believe, there is little correlation between the two. Yet although the range of temperature envisaged and the nature of the materials are different, there are many common problems which affect the field of both bodies and we cannot help thinking that better co-ordination would be useful.

It appeared at a Conference held by the E.R.A. a few weeks ago in London under the chairmanship of Sir Alfred Ewing, K.C.B., F.R.S., that funds for these researches are urgently needed. The sum asked for as a contribution from industry towards this work of extreme importance is only £1500, and we must suppose that it is only the severe pressure of the recent depression which has made it necessary to launch a public appeal for a sum relatively so small. The maintenance of British prestige and, if possible, of British leadership in this most important branch of engineering is of first-rate importance, not only as a national question, but to the industries concerned, and it is only by building up our own knowledge on a sound basis of research that such leadership can be achieved. As we have pointed out on many previous occasions, an industry cannot achieve leadership by following the footsteps of its rivals, and it is only those who are in the closest touch with research on new materials who have the best opportunity of realising the value of a new discovery and of appreciating the manner in which it can be applied. We trust and believe that the appeal for funds made at the Conference will not only be promptly met, but that considerably more than the sum asked for will be subscribed. There is room and need for much more, and both in the time occupied and in the width of field covered the industries concerned will profit more than proportionately from their contributions.

Accidents and Progress.

A PUBLIC speaker recently recalled the fact that once, many years ago, the steamship "Umbria" broke her propeller shaft in mid-Atlantic; when the causes of this accident came to be investigated one of those responsible for the investigation remarked that "if there were no accidents there would be no progress." One can, of course, see exactly what was in the mind of the author of that remark, who was, we believe, a well-known steel metallurgist, and there is a certain measure of truth in his saying. A serious accident undoubtedly leads to a degree of investigation which is not accorded to minor failures, and, moreover, attracts public attention to such an extent that "something has to be done about it." In that way, no doubt, the occurrence of an accident may well prove to be the beginning of an important advance.

On the other hand, it must be borne in mind that there are in engineering practice an immense number of failures and breakages which do not lead to accidents in the spectacular sense of the word, although they may cause serious loss of time and money. Unfortunately, in many of these cases the broken parts are removed as rapidly as possible, a replacement is effected, perhaps, by the use of a heavier part, or of a material supposed to be superior, and the whole incident is forgotten as quickly as may be. In some cases, of course, those who have suffered loss by a breakage seek to fasten the responsibility upon the maker of the article which has failed, or of the material from which it has been made, and the result is a species of controversy which, as a rule, turns more about the relative responsibilities of the parties than the technical merits of the case. The makers of materials in particular are often disinclined to enter upon any very searching technical investigation; only too often their main desire is to melt down the broken pieces in order that there shall be no possibility of anything, for which they can be held responsible, being discovered. No doubt, from a purely business standpoint, if one's view is confined to the transaction in hand, such a policy is understandable, but it is very unfortunate not only in the interests of engineering and metallurgical progress generally, but in the interests of the firm in question. In some cases the technical men concerned may believe that they know the reason for the failure and they may even be conscious that such a reason would not redound to the credit of their workmanship or material. Such knowledge, however, is frequently found to be based upon misconceptions, and investigations show that defects, which occasionally lead to failure, may have their origin in causes which the makers of the material do not in the least suspect. Defects no doubt occur in almost every piece of material; at all events if we apply the word in the strict sense. Fortunately, it is true that the great majority of defects do not in the least matter, because they do not lead to failure or deterioration. In view of the large factors of safety which are often employed, and of the margin for wear, corrosion and other deteriorating agencies which is generally allowed, it is not surprising that minor defects pass without attracting attention. Every now and then, however, such minor defects occur in a position where they become of major importance; sometimes a number of different features of an undesirable nature become superposed and trouble results. If such cases are investigated the maker's knowledge of his material becomes very much strengthened, and his attention is called to the importance of factors which, from long practice, he has come to ignore. In this way a study of failures can be made the most valuable stepping stone towards improved practice and improved materials. Nor is it essentially a question of the development of new materials, or of endeavouring to reach higher values in the physical properties upon which their uses are based. The sort of problem we have in mind relates rather to what may be termed the general quality of the material, which, in the long run, is very largely a question of uniformity and homogeneity. These terms, of course, represent ideals which are never entirely attained by practical materials, but the degree to which they can be approached varies widely with the methods of manufacture adopted, while there is also the consideration that the methods of using a material should take into account the peculiarities to which every metal and alloy is subject. It is in these regards particularly that both the engineer and the metallurgist can learn

very much from the careful and impartial study of cases of failure.

There is, however, another aspect of the study of failures which is at least equally important. Designers very frequently employ the cheapest material they can obtain which they believe will serve a particular purpose. When, subsequently, actual failures occur, their faith is shaken and instead of investigating the failures, they too often take the simple course of employing a stronger, although perhaps a slightly more expensive material. The range of alloy steels, for example, which modern metallurgy has provided, offers such possibilties of this order that a step of this kind could be repeated more than once before the possibilities were exhausted. It has been rightly pointed out that if used in this way the resources which modern metallurgy has provided for the engineer may become a hindrance rather than an aid to the improvement of design generally. The reason is, of course, that an easy way out of a difficulty offered by a stronger material apparently avoids the necessity for a close study of failures. Yet in many instances such a study would have revealed that the cause did not so much lie in the general character of the material, as perhaps in an error of design, such as the use of too small a radius at a fillet—or of no radius at all at an angle—or the presence of other features which provide a notch effect. Such errors of design are far better corrected by the application of well-known principles, *i.e.*, by the provision of larger radii and smoother outlines, than by the "brute force" process of employing a material capable of withstanding the unnecessarily severe conditions to which the existing design subjects it. Nor does it follow that a "stronger" material will necessarily overcome such a difficulty. The property known as "notch sensitiveness" is sometimes more marked in materials of higher tensile strength and higher elastic limit, and in such cases the designer may be driven by trial and error to the use of something softer and weaker. In this way it sometimes happens that prejudices are created against materials of high quality or in favour of others whose real powers in regard to fatigue endurance may be decidedly lower. Treated in this way cases of failure, so far from being an incentive to progress, may become an important cause of stagnation or even of retrogression. We see, therefore, that progress can scarcely be said to follow necessarily from accidents, but only from their exhaustive study, both by the skilled engineer and the skilled metallurgist.

Welding Non-ferrous Metals.

There can be no doubt about the progress which the welding of steel has made in recent years. The great conveniences which the process offers and its economy in cost and in weight of material had made its extensive adoption inevitable. Provided that the well-known drawbacks of welding are recognised, and adequate provision is made for them, the adoption of welding, in regard to structural steel at all events, constitutes a most important advance in our means of construction. The welding of non-ferrous materials, on the other hand, is a matter which, while it offers rather less commercial attraction, at the same time presents a series of difficulties which differ widely from those encountered in the case of steel. Further, these difficulties vary from one metal and alloy to another sometimes in a perplexing and even baffling manner. The welding of copper has been practised with considerable success, as, for example, in the construction of certain locomotive fire-boxes on Continental railways. Here the characteristics of the metal offer both advantages and difficulties. The high thermal conductivity of copper requires the supply of a much greater amount of heat, proportionately, than is needed for the welding of steel, while, if oxide is present in the copper, difficulties of another kind leading to porosity and other defects are encountered. With properly deoxidised copper which is now widely used, the worst of these difficulties disappear and there is little trouble to be feared either from grain growth or from the weakening effect of a critical or sub-critical temperature. The weld is, of course, soft, resembling in its properties the fully annealed metal rather than the material in the rolled condition as ordinarily employed, and this is a feature which must be allowed for in design.

The welding of pure aluminium also has proved satisfactory. Here the oxide skin on the surface of the metal introduces a difficulty, but this skin can be ruptured mechanically, and thereafter fusion welding becomes relatively simple.

Where alloys have to be treated, however, the non-ferrous materials offer some special difficulties. Perhaps the worst example from this point of view is that of alloys which have been improved in regard to their mechanical properties by heat treatment, frequently called "age-hardening." Such materials as duralumin, for example, cannot be welded without entirely destroying the beneficial effects of heat treatment. Only where the welded structure could afterwards be re-heated and quenched and allowed to age would it be possible to overcome this difficulty In addition, there is in the case of commercial materials an evolution of gas from alloys of this type during welding, and these gas bubbles tend seriously to weaken the joint. This defect may perhaps be overcome when it becomes possible to produce aluminium and aluminium alloys really free from dissolved gases.

Difficulties of another kind appear to occur in the welding, whether by electric arc or oxy-acetylene flame, of some of the stronger alloys of copper. Apparently alloys of the brass type, *i.e.*, containing considerable proportions of zinc, cannot readily be used as welding electrodes in the arc process, because they do not flow readily, and in many instances it is necessary to use phosphor-bronze as the welding metal for alloys of totally different composition. This is, of course, unsatisfactory, and it constitutes a serious obstacle to the extension of the welding process to these materials.

Numerous other instances of difficulties and defects arising in the welding of non-ferrous metals can be cited, but those quoted above are perhaps sufficient to show that further attention to the welding of non-ferrous metals is eminently desirable on the part of those concerned with the development of welding processes. It is true that the tonnages of non-ferrous metals to be welded are small compared with those of steel, but the value of the product is proportionately much higher and, consequently, can provide a satisfactory field for the application of welding.

In France an institution for carrying out investigations on autogenous (gas) welding has been established, but there does not appear to be a similar

organisation in Great Britain. In so far as investigations on welding are in hand in our public institutions and laboratories, they appear to be confined almost entirely to problems relating to structural steel. Not only in the interests of the welding processes, but in those of the non-ferrous metals themselves, attention to that aspect of the matter is desirable. It is perhaps one of those questions which the British Non-Ferrous Metals Research Association might well take into consideration as part of a future programme. There is at the present moment an appreciable measure of rivalry between steel, and more especially rust-resisting steel, and certain non-ferrous metals in a variety of applications. It is true, of course, that the rust-resisting steels also offer very special problems and difficulties in regard to welding, but these have received a large amount of attention, and if not already overcome are likely to be in the near future. Facility for jointing by a cheap and simple process is an important asset to any material, and the manufacturers of non-ferrous metals themselves would be well advised to realise that fact.

Quantitative Analysis by X-Rays.

ANALYSIS of matter can be carried out in two different ways by means of X-ray methods. In one of these use is made of the fact that each chemical element can be made to emit, by bombardment with electrons in an X-ray tube or by irradiation with X-rays, a characteristic X-ray spectrum, the wave lengths of which, when measured, serve to identify the emitting element. The wave length of the characteristic radiation of an atom is not affected by its state of chemical combination, so that, for instance, copper, either as the element or as oxide or other salt, or in solid solution, always yields the same X-ray spectrum. The advantage of the method over optical methods of spectrum analysis lies in the comparative simplicity of the X-ray spectrum, which consists of relatively few wave lengths. The method is exceedingly sensitive, and by intensity measurements can be made to yield quantitative results in certain cases.

The method of X-ray analysis can, however, be used in another way which yields an answer to a somewhat different problem which cannot always be solved by chemical methods. The problem in this case is to determine the relative amounts of two or more different crystal substances in a sample. This subject has been discussed at some length by Glocker,* who quotes, as an example, the case of a mixture of NaCl, KCl, and KBr. Chemical analysis will determine the percentages of sodium, potassium, chlorine, and bromine, but not, however, the amounts of the three salts. Problems of this type not infrequently confront metallurgists; cases in point being the elucidation of the structure of oxides consisting of more than one compound, and in the determination of the relative amounts of two phases of the same composition but different crystal structure. The method has been applied with success by Sekito† to the determination of the ratio of martensite to austenite in quenched steels.

Following Glocker's article, we will briefly consider the principles of the method and the difficulties of its application. The method depends on the possibility of calculating the quantity of scattering material present in a beam of X-rays from a measurement of the intensity of the scattered radiation. In practice, it is (for the present purpose) only the ratio of the scattered intensities due to two different crystalline materials that is required. A difficulty arises here at the very outset from the fact that crystals lie between two extremes, viz., the "ideal" and "mosaic." The first is a geometrically regular distribution of the atoms in space, and constitutes a unit in itself. The second consists of a very large number of small "ideal" crystals, all oriented in very nearly the same way. The intensity of the scattered radiation depends on the perfection of the crystal, so that to compare the quantities of two scattering crystals it is essential that their "mosaic" structures should be comparable, or that the regions of lattice homogeneity should be reduced (by cold working, for instance) to such an extent that the absorption of the incident beam in each region is negligible. In practice, this means that the units of the "mosaic" will have dimensions of the order of 10^{-5} cm., but this does not mean that a powder of this fineness has to be produced.

If the material can be obtained in a suitable state as outlined above, it is then mixed with a standard comparison substance of known scattering power, such as powdered aluminium, a Debye-Sherrer powder photograph obtained, and the intensities of reflection from the different crystal planes measured. If I_1 is the intensity of a diffraction line of the crystalline phase of which the material contains a proportion p_1 by weight, and I_2 is that of the comparison element, then for the simplest case in which each crystal consists of one kind of atom only

$$\frac{I_1}{I_2}=\frac{p_1\,\rho_1\,A_1^2\,K_1\,H_1\,L_1\,F_1^2\,\Sigma_1^2\,e^{-2M_1}\,n_2^2}{p_2\,\rho_2\,A_2^2\,K_2\,H_2\,L_2\,F_2^2\,\Sigma_2^2\,e^{-2M_2}\,n_1^2}$$

Where

$p_1\,p_2$ are the proportions by weight of the phases.
$\rho_1\,\rho_2$ the densities.
$A_1\,A_2$ the atomic weights.
$F_1\,F_2$ the atomic scattering factors.
$H_1\,H_2$ the frequency of occurrence of the crystal planes.
$L_1\,L_2$ the Lorentz factors.
$\Sigma_1\,\Sigma_2$ the structure factors.
$M_1\,M_2$ the temperature corrections.
$K_1\,K_2$ the absorption corrections.
$n_1\,n_2$ the number of atoms in the unit cells.

In this formidable array of variables, H and L are known, the former being a geometrical property of the crystal and the latter a function of the angle of reflection; ρ, A, and n are also supposed to be known. The remaining quantities, F, Σ, M, and K, are discussed at some length by Glocker. To illustrate the difficulties of the method, he cites the case of two mixtures of three parts by weight of aluminium with one part of iron, the iron being from two samples of different grain size (A and B). The ratio of the intensities of the (110) reflection in powder photographs taken with the K characteristic of copper ($\lambda=1\cdot54$ A°) gave $I_A : I_B = 0\cdot49 : 1\cdot0$, while photographs obtained

* "Metallwirtschaft," XII., p. 599, 1933.

† "Sc. Rep." Tohoku Imp. Univ., 20, pp. 313, 369, 377; 1931.

with molybdenum radiation ($\lambda = 0{\cdot}71$ A°) yielded $I_A : I_B = 0{\cdot}98_5 : 1{\cdot}0$, a result in reasonable agreement with the compositions of the two mixtures. The failure of the method when copper radiation was used is due to the very high absorption of this wave length in the iron. This example is sufficient to show the very great care required in applying the method; it might even be said to condemn it for practical purposes. It must, however, be remembered that the information yielded cannot usually be obtained by other methods. In cases such as the determination of the amounts of α and γ iron in a quenched steel, the application of the method is justified by the importance of the results obtained. As a general method of analysis its utility is evidently very limited, but in particular cases it may be of very great use.

Lubrication.

METALLURGY is distinctly a " borderland " subject, and many of the problems with which the metallurgist is confronted from day to day, in commercial application as well as in more academic investigation, require for their adequate consideration more than a nodding acquaintance with the results of quite recent work in other branches of science. This is exemplified in a marked degree by the study of bearing metals, to which characteristic and essential contributions are being made by metallurgists, engineers, physicists, physical chemists, and organic chemists. The range of activities thus involved introduces considerable difficulties in the way of the specialist who wishes to keep in touch with the work going on in other fields, and lends added interest to a competent review which co-ordinates as far as possible the information emanating from these various sources. An excellent example of this type of survey is provided by the article, under the same title as the present abstract, by Kyropoulos in *Metallwirtschaft*, Vol. XII., No. 5, pp. 62–64. Kyropoulos' own publications place him in a position of special authority to present such a review, but it is pleasing to see that due reference is made to the work done in Great Britain, America, and France, as well as Germany.

The author expresses the modern conception of lubrication in the view that the physical process which makes lubrication possible is the adsorption of the lubricant on the parts sliding or rolling over one another. It is between these adsorbed layers that molecular friction occurs, but the lubrication may be of the " hydrodynamic " or the " boundary " type, according to the constitution of the oil film.

Hydrodynamic or " full-fluid " lubrication prevails when a relatively thick layer of oil is present between the two adsorbed layers, and in this case theory, due chiefly to Petrow, Reynolds, and Sommerfeld, leads to an expression according to which the coefficient of friction in a plain journal bearing is a function only of the viscosity of the oil at the prevailing temperature, the surface area of contact, and the velocity gradient in the oil film. Owing to the manner in which the journal automatically shifts its position in the bush with increasing speed, there is a certain speed at which the coefficient of friction is a minimum. This minimum value depends only on the dimensions of the bearing, and cannot vary by more than about 6 per cent. from the value corresponding to a vanishingly low speed. It is important to note that in theoretically completely hydrodynamic lubrication the only property of a material involved is the viscosity of the oil; no account is taken of the nature of the metallic components of the bearing. Experimental investigations in this field have been devoted mainly to measurements of the coefficient of friction under varying loads and speeds, the thickness of the oil film, the excentricity of the journal in the bearing, and the distribution of pressure in the oil layer. When the postulates of the theory have been fulfilled these tests have generally given results in good agreement with its predictions, but discrepancies which have been observed have given rise to considerable discussion. Many of these supposed deviations have probably been due to failure to establish thermal equilibrium and the difficulty of determining accurately the temperature at the true bearing surface, but there are others of a more fundamental nature which arise from the neglect of the classical theory to take into account the fact that the viscosity of the oil is affected by the local pressure in the bearing as well as by the temperature. The shear gradient, du/dh where u is the velocity of the moving part and h is the thickness of the oil film, is also found to have an influence on the viscosity. A decrease in viscosity under a high shear gradient is to be expected if the molecules of the lubricant are very unsymmetrical. This effect is most marked with long rod-like or chain-like molecules, in which there is a strong tendency to oriented flow (" Strömungsorientierung "). Variations in viscosity from 7 to 17 per cent. arising from this cause have been observed, and the effect is likely to be still greater in the bearings of internal combustion engines running at the highest speeds, where very high shear gradients are encountered.

The state of boundary lubrication is attained in a bearing when the entire oil layer consists solely of the two adsorbed films. The frictional force is then proportional to the static coefficient of friction and the pressure of the moving member on the stationary basis. In contrast to the essentially chaotic movement of free molecules in hydrodynamic lubrication, boundary lubrication is characterised by a gliding of anchored molecules over one another, analogous to the gliding of crystal surfaces in the plastic deformation of metals. The adsorbed layer has a definite structure, which remains unaltered over a wide range of temperature, and forms with the surface atoms of the metal what must be regarded as a solid body. The orientation of the oil molecules in this boundary layer depends on their constitution, while the specific influence of the metal basis is manifested in the attractive force with which the layer is held. The definite function thus ascribed to the metal of the bearing is one of the most important distinctions between boundary lubrication and the hydrodynamic type.

Hardy has succeeded in demonstrating the influence of the metal on adhesion of the adsorbed film by means of direct tensile tests. Copper and iron blocks with optically plane surfaces were prepared and were " cemented " together in pairs consisting of copper to copper, iron to iron, and copper to iron, by placing between them molten organic substances such as palmitic acid and eicosan, which were then allowed to crystallise in position. When the force necessary to break down the adhesion of these composite blocks was determined, the adhesion between pairs of dissimilar metals was found to be approximately equal to the arithmetic mean of that between the pairs of similar metals. Rupture of the cementing layer

always occurred so that only a primary adsorbed film was left on one of the metal surfaces, as was shown by subsequent measurement of the static friction. In the case of composite blocks made up of two different metals, the primary film remained on the metal which showed the smaller adhesion when tested in conjunction with another similar block, thus indicating that the influence of the metal with the stronger attractive effect extended completely through the non-adsorbed portion of the cementing layer. Hardy's conclusions were confirmed by Trillat's X-ray investigation, while Büche's measurements of friction under boundary lubrication and of heat of adsorption, which gives a measure of the saturation of the field of force of the metal surface by the lubricant, showed that in different oils the "oiliness" was greater in those with the higher heats of adsorption.

From the standpoint of organic chemistry also, certain regularities present themselves. Hardy found that in the series of normal saturated paraffins the static coefficient of friction decreased linearly with increase in molecular weight, a discovery which can be understood as a consequence of the orientation of the molecules and the method of attachment to the surface of the metal. The coefficient shows the same sequence in the homologous series of alcohols and acids, and within any group of related paraffin-alcohol-fatty acid the coefficient is smallest for the acid and greatest for the hydrocarbon. This is a further indication that the polar compounds saturate the molecular field of the metal most strongly. The practical interpretation of this is that in comparing two lubricants the one with the greater dielectric constant will in general give the more effective saturation, the smaller friction and the greater protection against seizure. When the oil is a mixture of a normal hydrocarbon and a fatty acid (*e.g.*, undecane and caprylic acid) the final value of the coefficient of friction is only attained after a more or less prolonged period, and is then equal to that corresponding to the pure acid, down to very small concentrations—as low as 0·7 per cent.—of the latter. Time is required for the formation of the adsorbed film, because the acid molecules, originally in a chaotic condition, must arrange themselves in an orderly, oriented manner, since they attach themselves to the metal by their carboxyl radicles. In mixtures, such as those mentioned, of polar and virtually non-polar bodies, the principal cause of delay is the time necessary for the polar molecules to diffuse out of the mixture on to the surface of the metal.

The purely chemical investigation of oils has given valuable information on secondary effects, such as the tendency to oxidation and resistance to emulsification; but a serious obstacle to the elucidation of the constitution along these lines, especially as regards mineral oils, has been the mixed nature of almost all lubricants derived from normal sources. Observations on the physical phenomena of oriented flow, boundary lubrication and selective adsorption, and the accurate determination of physical properties, especially density, refractive index and specific refraction, appear to offer better prospects of success. Using these methods Kyropoulos himself has shown that the Pennsylvanian oils, which have a paraffin basis, consist most probably of a mixture of different isomers.

The list of references reproduced below gives some indication of the attention which is being devoted to the mechanism of lubrication. None of the aspects of the subject touched upon by the German author is unimportant to the metallurgist and engineer, but from their point of view, and with reference to immediate practical problems, special interest will be attached to further investigations on boundary lubrication, and particularly to work such as that of Hardy on the specific influence of various metals. A great benefit will be conferred on all concerned with the design, manufacture, and operation of bearings if a rational solution can be found for these problems, which at present have to be approached on almost entirely empirical lines.

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The Sharpness of Razor Blades.

IN the issue of *Metal Progress* for November, Mr. P. N. Peters, of New York, gives a very interesting account of this subject, and especially of one of the latest methods devised for measuring that elusive quality known as "sharpness." He begins by pointing out that the cutting action of a razor blade is very different from that of most cutting tools, since the majority of the latter act as wedges, which split or prise off the material, so that their action is dependent rather more upon the correct angle and durability of their wearing surfaces than upon the edge itself. The actual edge of the razor blade, however, has to force its way through the hair follicle, and if the shave is to be smooth and painless the edge must

do this without seriously bending or pulling the hair. The latter action is particularly objectionable if the path of the edge becomes deflected in the direction of the length of the hair, since this produces an unpleasant sensation of "pull."

The American author next considers what are the features of a razor blade which determine its cutting behaviour. He points out that the actual edge can be regarded as a minute semi-cylindrical surface of definite radius and curvature. He gives this radius as averaging from 10^{-3} mm. to 10^{-4} mm., or 0·00005in. to 0·000005in. Apparently, however, an actual edge is never a smooth semi-cylinder of this kind, but is divided up in a more or less jagged fashion into peaks and ridges depending upon the exact manner in which the edge has been finished, *i.e.*, grinding, stropping, or polishing. It seems to be the exact manner in which these irregularities are arranged which determines the behaviour of the blade in use; it must not be too smooth nor yet unduly rough. It is only when the "peaks" of the edge are so arranged that they attack the hair preferably from two sides at once that the "easiest" shave can be obtained.

The problem of finding a means of testing the sharpness of a razor blade has received a good deal of consideration in recent years. Microscopic examination is unsatisfactory because, small as it is, the actual edge has a definite depth and a high-power microscope objective can never give a satisfactory image of the whole arrangement. The American author suggests that transverse sections would be needed, but he is apparently unaware of the fact that so long ago as 1906 Rosenhain, in this country, published some quite satisfactory photo-micrographs of cross sections of a razor blade. Instructive as cross sections are, however, since they require the destruction of the blade they clearly cannot be used for routine testing. In practice, safety blades are generally "tested" by examining the edges of a large number of them placed together in a block in an obliquely incident beam of light. Blades which have edges which are too rough or too smooth, or have a "wire" or "bur," can be picked out to a certain extent from the nature of the reflection which their edges give in such circumstances, but the test is necessarily very imperfect. A skilled workman who sharpens these blades is able to form some opinion as to the quality of the edge either by cutting a hair or by feeling the edge with a finger. The ultimate test, however, is still the subjective opinion of the user in actual shaving.

The quantitative tests hitherto devised do not, in Mr. Peter's opinion, approximate sufficiently to the normal conditions under which the blade acts in shaving. Thus the test devised by Honda and its development involve a kind of "hacksaw" action of the blade on successive layers of paper and would seem to be a means of determining the durability of the blade rather than its sharpness, and under conditions of cutting totally different from those of shaving. A better type of test is that in which the pressure required to cut a thread is measured, but here there is the great difficulty of securing a standard thread of uniform strength and thickness. Also in these tests the blade is generally pressed steadily downwards on the thread without any movement at right angles to the latter.

As a novel alternative to these Mr. Peters describes a test on razor edges by means of the corona discharge. It is, of course, well known that when an electrostatic charge of high voltage is placed upon a metallic body there is an electric discharge from any projecting sharp point, and it is believed that for a given voltage the amount of electric discharge increases with the sharpness of the point. An electrical arrangement is described whereby the razor blade is kept at a high voltage (6000 to 7000 volts) while one of its edges is set parallel to and at a short distance from a cylindrical metal bar. Across the gap between these two the corona discharge takes place and its amount can either be measured by means of a galvanometer or estimated by eye. Mr. Peters suggests that the ideal blade, being one with just sufficient roughness of the edge, gives a medium amount of discharge and that blades giving less than this are too smooth and those giving more are unduly rough. Apparently, after it has been used, a good blade becomes increasingly roughened. Mr. Peters ascribes this to the accumulation of corrosion products upon the edge and suggests that stropping of the surface restores the condition of the blade by the removal of this corrosion product. He suggests that this process is more perfect if the corrosion product is allowed to become rather thicker by the lapse of several days than if it is attacked at once. In this way he endeavours to account for the belief that better results are obtained if the same razor blade is only used at intervals of a week. While no doubt corrosion must play an important part in the behaviour of razor blades, there are also other phenomena arising from the local flexure of the very thin steel close to the edge which have to be taken into account before a full theory of the action of a razor blade can be achieved.

The Microscopic Study and Control of Electro-Deposition.

MESSIEURS A. PORTEVIN and M. Cymboliste describe in an article in *Revue de Metallurgie*, August, 1933, the technique for the successful use of the microscope in studying electro-deposited coatings, and in a series of photographs illustrate in a striking manner the way in which the structure is influenced by variations in the methods of depositing. These authors consider that insufficient use has in the past been made of the microscope for the study of electrolytic coatings, and this they believe applies both in the case of thick deposits, such as are met with in the production of electrotypes, and in thin deposits used for the decoration or protection of metal surfaces.

In their paper they show how the commoner types of defect arise, and in this way indicate the steps that should be taken for their avoidance; but they also show, probably for the first time, a series of photographs indicating the gradual change in structure that accompanies an alteration in any single factor of the depositing process.

PREPARING THE SPECIMENS.

The chief difficulty in dealing with thin coatings is the mounting and polishing of the specimens. For simple examination of the surface itself, either as deposited or after polishing, there is no particular difficulty, but for cross sections (which are more generally informative) some method of protection and support for the coating is needed prior to polishing. It is particularly important to avoid rounding the edges. Any of the better-known methods of protection may be employed, such as embedding in a fusible alloy or wax or one of the plastic materials, such as bakelite; or, again, the surface may be pro-

tected by a relatively thick coating of another metal applied electrolytically, nickel and chromium being particularly useful in this direction. The importance

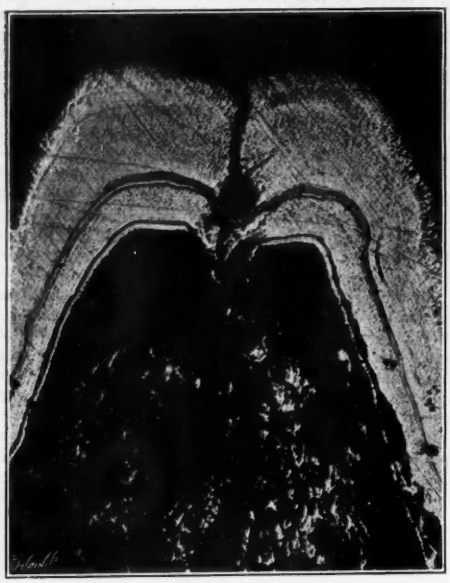


FIG. 1—× 170. *Etched in Pure Nitric Acid. Porosity in a Nickel Deposit due to a works defect at the peak of a screw thread. This fault was repeated in each thread.*

of careful mounting is emphasised by the fact that with thin deposits magnifications as high as 2000 are often necessary. In choosing the protecting or embedding material it is necessary to bear in mind the etching agent which is to be used, as this will have its effect on the protecting medium as well as on both the deposit and the base metal. It is frequently a help for this reason to use an alcoholic base for the etching reagent. Where electrolytic interference is anticipated this may sometimes be overcome by using so powerful a reagent that the electrolytic effect is relatively unimportant.

MEASURING THE THICKNESS.

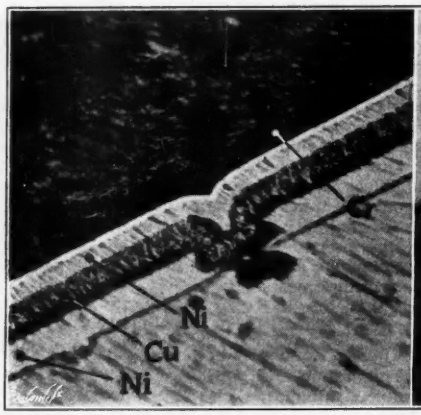
The usual methods of testing the thickness of the deposit are not really satisfactory, since in nearly all cases they give only the average thickness. This applies to all those methods in which the deposit is removed, and either weighed or estimated. From the practical standpoint it is the minimum thickness which is of importance, and this can most satisfactorily be shown by microscopic examination of a cross-section.

It can be readily understood that resistance to corrosion depends not on the average thickness but on the spots where the deposit is thinnest. Uniformity of thickness depends largely on the throwing power of the solution, but pinholes and porosity of all kinds, which tend to become exaggerated with increased thickness, can also be considered as spots where the thickness is below the average.

DEFECTS.

The authors distinguish between different types of defect, naming as the commoner faults, porosity (including pinholing as a special type of porosity), roughness or ridginess of surface, and peeling or bad adhesion.

Porosity or minute failures of the deposit at scattered points can be produced in many ways. Such defects may be due merely to an insufficient thickness of the coating and can then be easily overcome. They are, however, more often due to the presence on the cathode surface of minute non-conducting particles which may derive from impurities held in suspension in the bath. Defects in the basis metal may cause failures of this type, and photomicrograph No. 1 shows a pore which has arisen from this cause.



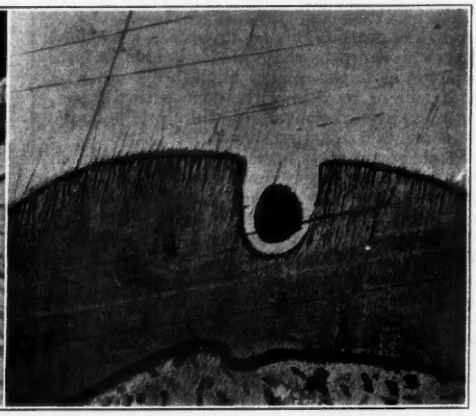


FIG. 2 **FIG. 3**

FIG. 2—× 500. *Porosity in the Primary Nickel Coating due to a defect in the steel base. This porosity is completely covered by a copper deposit and the second nickel coating is of regular thickness as is the final chromium coating.*

FIG. 3—× 170. *Pinhole Open.*

In addition to the more obvious remedies, such as thorough filtering of the electrolyte and careful preparation of the cathode surface, the authors show that one of the most useful devices is to deposit an intermediate layer of another metal. As an example, a thin coating of copper may be made on a first coating of nickel, and then a final coating of nickel on top of the copper. Fig. 2 shows in what a remarkable way such an intermediate layer of copper can completely bridge over defects in the first nickel coating, so that the second nickel coating is free from any defect. Defects tend to grow when increasing the thickness of a coating of any particular metal, and even where a deposit is repolished and plated again there is always a marked tendency for defects to persist and become exaggerated. With alternate coatings, however, faults are generally covered up and eliminated. Another interesting result of the use of alternate coatings is that crystal growth is suppressed, and that consequently a thick coating can be obtained having a very fine structure.

Pinholes arise from hydrogen bubbles which form and adhere to the cathode surface during electrolysis. These bubbles result from unsuitable composition or concentration of the bath or from the use of too high a current density, or from the presence of dissolved gas. Their formation can be prevented by proper control of the conditions of working, and particularly by assuring a sufficiently high concentration of metallic ions. Individual baths are adversely affected in this respect by specific impurities in the electrolyte, an example being the presence of zinc in a nickel-plating bath.

Pinholes may in time be completely covered over by the growing deposit and Figs. 3, 4, and 5 show three stages in this process.

Many methods of testing for porosity and pinholes are in use, and, speaking generally, only the slower tests will distinguish between the two types of fault. Reagents are chosen that will attack the basis and not the deposited metal, preferably with the formation of a coloured product.

Cracks are only found in coatings which have poor ductility and may arise either during subsequent manipulation or bending, or may be produced spontaneously as the result of internal stresses.

While it is not always possible to produce a smoothly brilliant surface, it is always desirable to avoid roughness or ridginess, and especially isolated nodules. These usually arise from insoluble conducting matter present in suspension in the bath which may be carried over from the anode to the cathode, and, being covered over as the deposition progresses, give rise to roughness and unevenness.

Roughness may also be caused by unsuitable operating conditions, particularly low conductivity and too high a temperature of the bath. Increasing the current density usually leads to refinement of the crystal size until a point is reached where the crystals begin to grow apart, as is shown in Fig. 6.

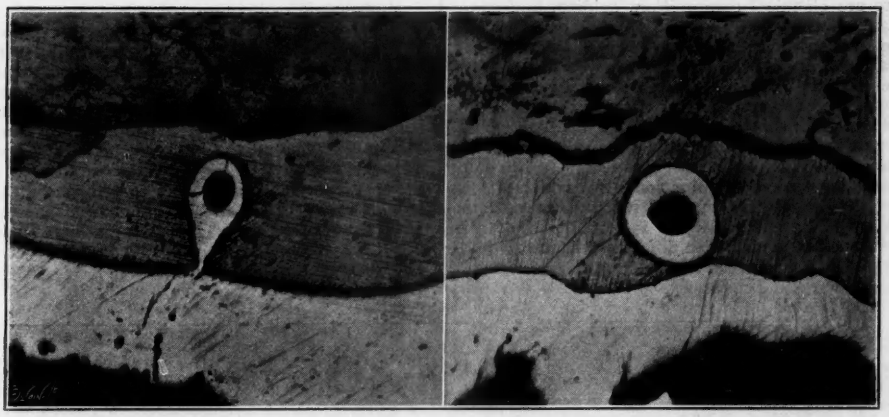


FIG. 4—× 170. *Pinhole Almost Covered Over.*

FIG. 5—× 170. *Pinhole Completely Covered Over.*

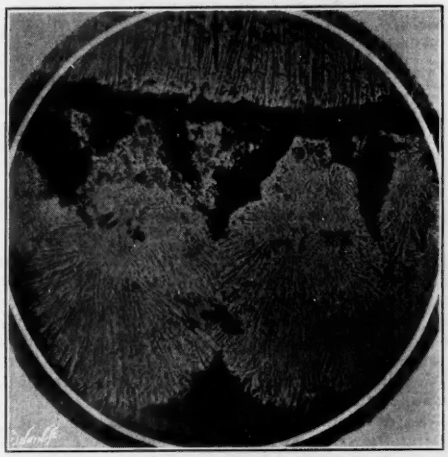


FIG. 6—× 350. *A Deposit of Copper at the Maximum Permissible Current Density followed by a deposit at a current density greater than this maximum.*

MEASUREMENT OF MECHANICAL PROPERTIES.

Mechanical properties are difficult to assess on the thin coatings generally met with in plating work and

the authors have therefore confined their tests to deposits sufficiently thick to strip easily and to be tested by any of the standard methods for hardness, ductility, tensile strength, elastic limit, &c. Pointing out that hardness in a deposit is usually accompanied by brittleness and softness by ductility, they indicate that the chief factors governing mechanical properties are chemical composition, acidity, and temperature of the bath, and the current density. In particular, lowering the temperature tends to increase the hardness and raise the elastic limit.

Microscopic examination, particularly of cross sections, shows the crystal structure of the deposited metal and from this it is possible to infer the mechanical properties, even in coatings too thin for direct testing.

Discussing micro-examination, by which it is intended to judge the crystal structure, the authors point out the great variety of information that can be obtained by etching with different reagents.

Of particular interest are photographs 7 and 8. can be used for this purpose. For this test, however, it is necessary to employ specially prepared test pieces. A practical method of checking, whether adhesion is satisfactory or not, is based on the observed fact that when hydrogen is liberated by electrolysis on a deposited coating the deposit will lift at any points where adhesion is poor.

Microscopic examination can also be used in the interpretation of adhesion problems in those cases where there is an intermediate layer preventing proper contact between the coating and the base. In cases of perfect adhesion microscopic examination shows continuity of crystal structure. It has often been observed that where, for example, a copper plate has been carefully etched so as to expose the crystal surfaces, these crystals will, if copper is deposited upon them, grow so that it is impossible to tell where the new copper starts. The authors point out that in some cases where one particular metal adheres badly to another, the trouble may be overcome by an intermediate layer of a third metal.

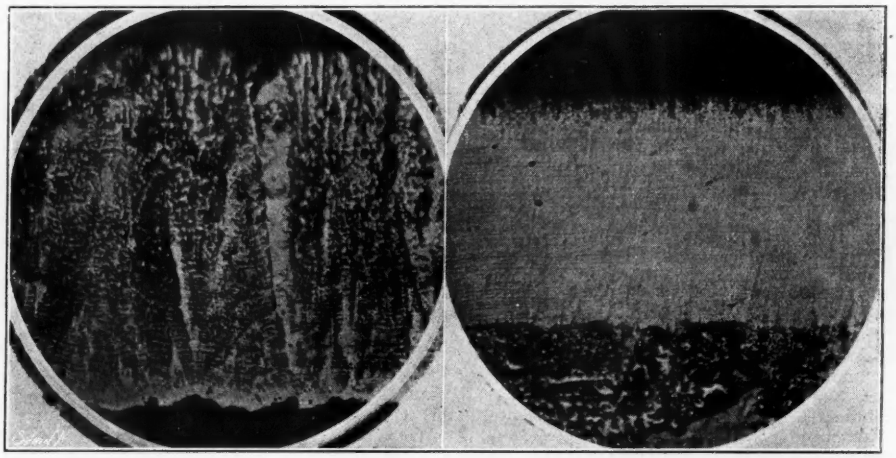


FIG. 7—× 500. *Nickel Deposited from a Sulphate Bath without Sodium Sulphate Additions.*

FIG. 8—× 500. *Nickel Deposited from a Sulphate Bath containing Sodium Sulphate.*

These show deposits of nickel prepared under conditions which were kept as similar as possible, with the exception that in the case of the deposit shown in Fig. 7 sodium sulphate had replaced a part of the nickel sulphate in the electrolyte. It will be seen that the structure has been entirely changed by the presence of the alkaline salt with the same anion as that of the metallic salt.

The development of the crystals is favoured by raising the temperature of the electrolyte and this effect is very marked in dilute solutions.

Good adhesion between coating and base is one of the most important factors in practical plating. Preparation of the cathode surface must be such that there will be no intermediate layer preventing direct and intimate contact between cathode and coating. Every trace of grease, impurity, oxide, or gas must be eliminated if good adhesion is to be obtained. Under perfect conditions adhesion may approach molecular attraction. Adhesion may be measured directly by finding the pull necessary to separate coating from base and the very delicate test suggested by Ollard

Closely bound up with adhesion is the question of stripping. This may appear as blisters or sometimes the whole coating may become spontaneously detached. In such cases high internal stresses have been added to poor adhesion. Such stresses can be caused in many ways, and can be reduced by careful attention to p H, current density, temperature, and other working factors.

Several methods have been put forward for measuring the values of these stresses, notably that of Mills, in which he deposited metal on the bulb of a thermometer, the contraction of the deposit being shown by the movements of the mercury. Marie and Thon measured the bending of a thin flexible cathode of which one surface had been insulated. Measuring the curvature gives a value for the stress. The microscope cannot give any direct evidence of the presence of stresses, except as these are reflected in irregularities and defects in the structure.

On the question of resistance to corrosion, the authors again emphasise the great value of alternating coatings of different metals. In superimposing

two electrolytic deposits of the same metal, the second, as has already been pointed out, often reproduces the failures of the first. There is, in fact, a certain heredity in faults and in structure. On the other hand, as is shown in Fig. 2, this heredity can be arrested by the use of successive coatings of different metals, which not only serve to cover up pinholes and other defects, but bring about, if the thickness of the intermediate coatings is sufficient, discontinuity of crystal growth which tends to produce a smooth surface with a small crystal structure. Multiple coatings of this nature have, the authors claim, better mechanical properties and much improved resistance to corrosion, as compared with single coatings.

The use of multiple coatings appears to offer a wide field for further investigation.

Oxygen and Oxides in Iron and Steel.

No. I.

IN their paper "Present Position of Methods of Analysis of Oxygen and Oxides in Iron and Steel" (*Rev. Met.*, Nos. 8, 9, 10 and 11, 1932), Castro and Portevin present a summary of the present state of knowledge on this subject.

Le Chatelier and Bogitsch (*C. Rendus*, 167 (1918), page 472) early suggested the existence of a solid solution of oxygen in steel, and gave a value of 0·15 per cent. of oxygen in solution deduced from macro etching methods, but did not state the method used for the estimation of the oxygen. Rosenhain, Hanson and Tritton (*J.*, Iron and Steel, 110 (1924), pages 85–110) found a solid solubility of oxygen in iron of about 0·05 per cent. Oberhoffer, Schiffler and Hessenbruch (*Arch. Eisenhüttenwes.*, 1 (1927–28), page 57), by methods similar to those of Le Chatelier and Bogitsch, arrived at a value of 0·05 per cent. Schenck and Dingmann (*Z. Anorg. Chem.*, 164 (1927), page 133), by studying the equilibrium between iron oxides and mixtures of carbon monoxide and dioxide, obtained the very high value of 2·8 per cent. oxygen at 1100 deg. Cent. The accuracy of this value was challenged by Benedicks and Loefquist on the grounds of the reaction between the iron oxide and the alumina boats used in the experiments. Schenck, Dingmann, Kirscht and Wesselcock (*Z. Anorg. Chem.*, 182 (1929), pages 97–117), using iron instead of iron oxide in the gas equilibrium method, obtained a solubility of 0·4 per cent. oxygen at 1000 deg. Cent. Gries and Esser (*Arch. Eisenhüttenwes.*, 2 (1928–29), page 749) found that they could not produce single crystals from iron containing more than 0·055 per cent. of oxygen. Wasmuht and Eilender (*Arch. Eisenhüttenwes.*, 3 (1929–30), pages 659–64) deduce from age-hardening experiments a limit of solubility of 0·06 per cent. between 0 deg. and 680 deg. Cent., but neglect the influence of nitride and the effect of the small amount of carbon present in modifying the conditions of precipitation. Treinen (*Dr.-Ing. Diss. Aachen*, 1929), by methods similar to those of Le Chatelier and Bogitsch, finds a value between 0·060 and 0·065 per cent. oxygen and tempering experiments indicated an increasing solubility with rise in temperature. Krings and Kempkens (*Z. Anorg. Chem.*, 183 (1929), pages 125 and 190 (1930) and pages 313–20) in equilibrium experiments between iron and its oxides and mixtures of hydrogen and steam obtained a value of $0·11 \pm 0·015$ per cent. at 715 deg. Cent. Duenwald and Wagner (*Z. Anorg. Chem.*, 199 (1931), pages 321–346), from a study of the equilibria between carbon monoxide, dioxide and sheet iron, find a solubility below 0·01 per cent. at 800 deg. and 1000 deg. Cent. Ziegler (Preprint, A.S.S.T., Sept., 1931) heated test pieces in an oxygen atmosphere for periods varying from half-an-hour to two hours. There is no increase in oxygen content below 700 deg. Cent., but between 700 deg. and 900 deg. Cent. the value increases and the increase is more rapid above 900 deg. Cent., reaching a value of 0·1 per cent. at 1000 deg. Cent. Moreover, he states that the solubility is greatly lessened by the presence of carbon even at high temperatures. The length of the heating period, however, appears to be too short to attain equilibrium, especially at the low temperatures, as the oxide layer has a tendency to hinder the further penetration of oxygen. Schenck and Hengler (*Arch. Eisenhüttenwes.*, 5 (1931–32), pages 209–14), in experiments on the diffusion of ferrous oxide in iron in a neutral atmosphere, show that saturation, up to 0·2 per cent., is only obtained after 600 hours, a degree of diffusion much less than that indicated by Ziegler. Summing up, nearly all the authors find that the solubility of oxygen in iron is low, but their values are somewhat divergent. The limits of solubility may be accepted as less than 0·05 per cent. oxygen at room temperature and 0·10 per cent. at 900 deg. to 1000 deg. Cent. These limits may be considerably reduced by the presence of impurities, particularly carbon. The solubility of other oxides, such as manganous oxide, silica, &c., is probably very small and even negligible, for, as pointed out by Le Chatelier, the oxides are generally practically insoluble in metals other than their own constituent metal.

The solubility of oxygen in iron at the melting point may be accepted from the results of a number of workers as close to 0·22 per cent. Le Chatelier and Styri (*J.*, Iron and Steel, 1923, page 189) have pointed out that the presence of carbon greatly diminishes this solubility. From the results of Herty and his co-workers, Field (*Tech. Pub.*, A.I.M.M.E., No. 111 (1928)) and Vacher and Hamilton (*Tech. Pub.*, A.I.M.M.E., No. 409 (1931)) the value for $K_{Fe\,O \times C}$ in the reaction

$$FeO + C = Fe + CO$$

may be accepted as 0·011 at 1620 deg. Cent. Very little work has been done on the solubility of oxides other than ferrous oxide in liquid steel. Koerber (*St. u. E.*, 52 (1932), pages 133–144) has shown in the study of the deoxidation of iron by manganese that the solubility of manganous oxide is negligible.

The oxide inclusions most frequently met with in steel are oxides of iron, manganese, silicon, and aluminium. They seldom occur in the free state, but are usually in the form of silicates and combined or in solid solution with sulphides, &c. On account of their small quantity and especially their very complex composition they are very difficult to identify.

Methods for the estimation of occluded or dissolved oxygen in iron and steel may be divided into four principal groups: (*a*) drilling under a liquid layer; (*b*) solution in a reagent; (*c*) heating in a vacuum; (*d*) melting in a vacuum. Under method (*a*) water, oil and mercury have been used. Water gives rise to dissociation phenomena. Nearly all the authors find only a very small amount of oxygen, principally in the form of carbon monoxide. This fact is interesting, but the process has no quantitative value.

Method (*b*) consists in dissolving the metal in a reagent which gives theoretically no gas by reaction and collecting the gas which is released. There are various modifications of this method, but Klinger (*St. u. E.*, 46 (1926)) finds them to be unreliable and they are seldom used.

Method (*c*) is very old. It was first employed by Cailletet (*C. Rend.* 61 (1865), page 850), and Graham ("*Proc.*," Roy. Soc., 15 1866–67), and has since been used by many workers. Nearly all these agree that the extraction of gas is never complete, but that on heating to a higher temperature more gas is evolved. Large quantities of carbon monoxide and dioxide found are accounted for by the reduction of oxides in the steel or reaction tube by the carbon present. The results of experiments on the saturation of steel with carbon monoxide and dioxide at high temperatures and pressures can be attributed to simultaneous oxidation and carburisation of the metal.

Melting in a vacuum was employed by Austin (*J.*, Iron and Steel, 1912, page 236–41). He heated metal rods by an electric current to the melting point, and avoided contact with a refractory. Goerens and Paquet (*Ferrum* 12 (1915)), added a mixture of tin and antimony to the steel in order to form an alloy which was fusible at a moderate temperature.

Alleman and Darlington (*J.*, Frank. Inst., 185 (1918)) employed a molybdenum heating element and temperatures up to 1900 deg. Cent. in glazed alundum crucibles. They are the only workers to find free oxygen in the evolved gases, but are unable to prove that this is not due to the dissociation of carbon monoxide. To sum up; with all the above processes, it has not been possible to prove beyond doubt the presence of free oxygen. If oxygen is present it can only exist in the form of carbon monoxide or dioxide in visible flaws or in the form of simple or complex oxides.

The second part of Castro and Portevin's publication deals with methods for the determination of total oxygen irrespective of the form in which it is present. Hydrogen reduction methods, although not strictly of this type, are examined. Mention is made of the well-known Ledebur method and the many modifications and improvements chiefly due to the researches of Oberhoffer and others. Oberhoffer evacuated the apparatus in order to assist in removing oxygen and moisture. He also, with Keil (*St. u. E.*, 40 (1920), and 41 (1922)), adapted Wüst's method of adding an alloy of tin and antimony in order to effect the reduction of manganous oxide at a lower temperature. Maurer (*St. u. E.*, 42, 1922) showed that carbon present in the metal assisted in the reduction of the oxides. Rooney (*J.*, Iron and Steel, 110, 1924) studied the estimation of oxygen in pure iron. He considered that the reduction of the oxide by hydrogen depends more on the ease with which the water formed escapes than on the ability of the hydrogen to penetrate the metal. Also, he showed that the alloy method gives somewhat lower values than direct reduction of fine millings at 1150 deg. to 1200 deg. Cent. One of the most important facts, however, is the ease with which silica is reduced by hydrogen in the presence of iron at about 1200 deg. Cent. Oberhoffer and Keutmann (*St. u. E.*, 46, 1926, page 1045–49), and also Jordan, Eckmann and Jominy (*Sci. Pap.*, Bur. Stand., No. 514 (1925)), demonstrated the influence of the form of the sample. Fine millings tend to absorb oxygen and moisture. Thanheiser and Müller (*Mitt. K.W.*, 9, 1927) determined the effects of increasing silicon content on the course of the reduction. They found that with silicon above 0·2 per cent. reaction with ferrous or manganous oxide occurs and the silica formed is not reduced by hydrogen. Petersen (*Arch. Eisenhüttenwes.*, 3 (1929–30)) employed a nickel catalyst to estimate carbon monoxide and dioxide formed during the reaction:

$$CO+3\,H_2=CH_4+H_2O$$

$$CO_2+4\,H_2=CH_4+2\,H_2O$$

He showed that the reducing power of carbon increases and that of hydrogen diminishes at increasing temperature. To sum up very briefly; the applicability of the hydrogen reduction method is limited.

The hot extraction method was used by Walker and Patrick (*Inter. Cong. Appl. Chem.*, 1912, Vo. 21, page 139–48), who employed a spiral graphite vacuum furnace. It was abandoned on account of experimental difficulties.

Oberhoffer and his colleagues (*St. u. E.*, 42 (1922), and 44, 1924), used a Swedish cast iron to supply the carbon for reduction purposes and an antimony-tin alloy to lower the melting point to below 1200 deg. Cent. Heating was carried out in a carborundum resistance furnace. Later a molybdenum wire-wound furnace was employed giving temperatures up to 1800 deg. Cent., and thus rendering possible the reduction of the more refractory oxides. Reduction of the boat material also occurred and the method was abandoned. Strauch and Oberhoffer (*St. u. E.*, 45, 1925) used a cast iron containing 4·3 per cent. of carbon and 0·45 per cent. of manganese instead of the antimony-tin alloy to lower the melting point of the steel. They used millings in the case of steel and solid test pieces in the case of cast iron. Oberhoffer and Hessenbruch (*St. u. E.*, 46, 1926) studied the reduction of various oxides in powder form contained in iron capsules. They decided that boats of refractory material should be replaced by graphite crucibles. Jordan and Eckmann used a high-frequency induction furnace, solid test pieces and gravimetric analytical methods. A high pressure was generated in the furnace by the slow passage of the gas through the absorption tubes. The reduction was carried out at 1550–1600 deg. Cent., and both refractory and graphite crucibles were used. Hessenbruch and Oberhoffer (*Arch. Eisenhüttenwes.*, 1, 1927–28) pointed out that additions of manganese and aluminium caused a decrease in the quantity of oxygen extracted. They also showed that it was impossible to work at temperatures above 1400 deg. Cent. with refractory boats. After the publication of the work of Jordan and Eckmann they experimented with a high-frequency furnace. They introduced a method for dropping the samples into the crucible in order to avoid releasing the vacuum for each estimation. They noted the deposition of manganese and aluminium on the cold parts of the tube, and attributed the disturbing action of these metals to the reabsorption of carbon monoxide by the finely divided metallic films. They therefore recommend the rapid extraction of the gases.

Von Seth (*Jernkon. Ann.*, 112 (1928)) devised an excellent high-frequency, furnace prototype of the best small capacity furnaces used to-day. He eliminated all refractories in the furnace and supported the crucible on a graphite rod. He confirmed the absorption of carbon monoxide by the manganese deposited on the walls of the tube. Diergarten (*Arch. Eisenh.*, 2 (1928–29)) experimented with other types of furnace, using silit rods or a spiral of molybdenum or

carbon. He also made use of a double vacuum arrangement. He inserted a sheet of molybdenum between the magnesia screening crucible and the graphite crucible. An electro-magnet was employed for dropping the samples into the crucible. Thanheiser and Müller (*Mitt. K.W.*, 11, 1929) made experiments on the reduction of oxides using a high-frequency furnace excited from a rotary generator. They used a maximum temperature of 1500 deg. Cent., and obtained a reduction of 70 per cent. for silica and 25 per cent. for alumina. Vacher and Jordan (*Bur. Stand. J. Res.* 7 (1931)) used a similar apparatus to that employed by Jordan and Eckmann, but with some modifications. The principal modifications are in the vacuum pump and the collection of the gases in reservoirs from which they are circulated through the analytical apparatus. They find that 0·24 per cent. manganese causes errors and that 0·05 per cent. of aluminium in the presence of manganese is troublesome. Bardenhauer and Schneider (*Mitt. K.W.*, 13 (1931) used a high-frequency furnace of the von Seth type. They concluded that alumina or aluminates present in the steel in a finely divided state are completely reduced by carbon, slowly at 1500 deg. and much more rapidly at 1600 deg. Cent. They consider the maximum limits for manganese and aluminium to be 1·0 and 0·5 per cent. respectively; but that alumina is not reduced by carbon in the absence of iron.

The Alloys of Iron with Aluminium.

IT would almost appear to be a commonplace to say that any alloy system which has been shown by the early physical metallurgists to be a simple one has been incorrectly shown, while those that appear to be moderately complicated are really very complex. The alloys of iron and aluminium are an example of the latter case. The system was first investigated just a quarter of a century ago by Gwyer, and appeared to be comparatively simple. Later workers added complications, Gwyer himself returning, in collaboration with Phillips, to the study of the system in 1927, since which date several other workers have published diagrams of the series, the latest being due to Osawa.* In addition to direct investigation of the system, it has often been indirectly and unwillingly noticed by workers on other light alloys. The purest aluminium obtainable until comparatively recently contains appreciable amounts of iron, and the eutectic arrest of the system appears in the thermal curves of other aluminium alloys.

The diagram published by Osawa is given in Fig. 1. It is based mainly on the work of the earlier investigators (preference being given apparently to the results obtained by Gwyer and Phillips), supplemented by an X-ray analysis and microscopic examination of some thirty-five specimens lying between 40 per cent. Fe and 95 per cent. Fe, together with an X-ray examination of twelve alloys in the α-phase area.

The results are very difficult to criticise owing to the scanty amount of detail as to treatment which is supplied by the author. Thus, no reference is made to the condition in which existed the alloys submitted to the X-ray treatment—presumably, they were furnace cooled, but this is not stated. The same applies to the microscopic examination where in general the specimens are described as "annealed" or "rapidly cooled." From the text it would appear that the annealing consisted of a five-hour treatment at 1050 deg. Cent., followed by slow cooling, although whether this cooling time was measured in minutes or days is not specified. In addition, the photomicrographs reproduced suggest that seven alloys were quenched from between 1130 deg. and 1150 deg. Cent. If this represents all the work that was done, and it must be admitted that this appears to be the case, it forms a very unsatisfactory basis for establishing the solubility limits in a complicated system such as the one under examination.

The X-ray results obtained over the α-phase area are plotted in Fig. 2. The value given for iron (2·854 A) is lower than the generally accepted figure, which is 2·860. Perhaps this is not surprising in view of the fact that for the 100 per cent. Fe the author

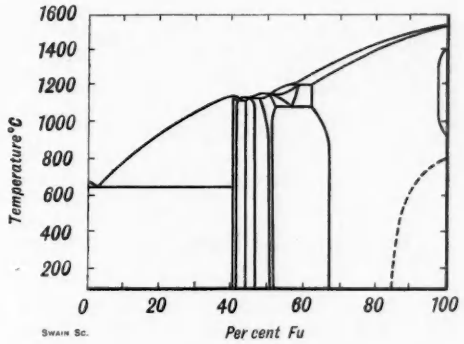


FIG. 1

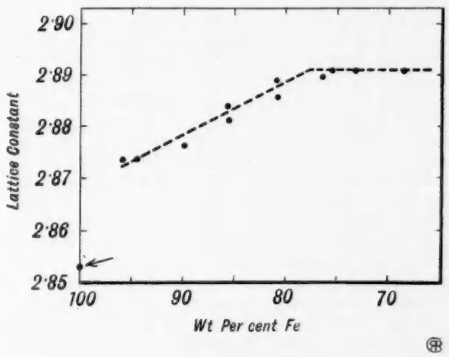


FIG. 2

* A. Osawa, "On the Equilibrium Diagram of the Iron-Aluminium System," Sc. Rep., Tohoku Imp. University, 1933, Vol. 22, p. 803.

used piano wire. From these results it would appear that the solubility limit of the α phase occurs at about 75 per cent. Fe. Unfortunately, nothing is stated as to the condition in which these alloys were examined, so that the temperature represented by this solubility limit is indeterminate. If, as might readily be assumed, they were slowly cooled to room temperature, the figure given (75 per cent.) does not agree with the author's diagram, nor does his description of the results fit in with the curve. Brevity is doubtless a great virtue, but the author has carried it so far as to render his results of no value unless one is prepared to accept his diagram without question.

Surface Compression and Corrosion Fatigue.

THE November issue of the *Zeitschrift für Metallkunde* contains an interesting paper by Föppl, Behrens, and Dusold on a series of corrosion-fatigue experiments in which they have tested the effect of surface compression applied to test pieces afterwards subjected to corrosion-fatigue conditions. Unfortunately, the manner in which this surface compression has been applied is not described, but it may be recalled that in previous experiments when Föppl showed the effect of "surface compression" in raising the apparent fatigue limit in a Wöhler test, this surface compression was obtained by lightly hammering the specimen over its entire area. Presumably some similar treatment has been given in the present case.

The materials employed in the present investigation comprise a number of German standard steels, such as St 37, V 2 A N, Nitriding Steel, S N-nickel steel, and electro-chromium-nickel-tungsten steel. In addition, pure nickel and aluminium alloys were also used, but none of the more important aluminium alloys, such as Duralumin, "Y" alloy, or M G 7 was included.

The method of fatigue testing adopted consisted in the use of a machine of the Föppl-Busemann type, where in one case torsion oscillations were employed, and in the other bending oscillations. In both cases stress on the specimen was ascertained from the amplitude of the oscillations, and although in some instances numerical values for endurance ranges are given, the results are plotted in terms of the amplitude of oscillation which a given specimen would withstand, usually for a million cycles, although in some cases the tests were carried to 10 million cycles. Tests were made in the condition as received in air, after surface compression in air, and in the condition as received in water, and after surface compression in water. Corrosion-fatigue conditions, however, differ somewhat from those generally employed because the water, instead of being allowed to flow on the specimens in a jet, was made to surround them completely by means of an envelope or outer vessel consisting of glass tube and india-rubber. This arrangement made it possible to observe corrosion phenomena during the progress of the test.

While it must be regarded as unfortunate that the German authors have limited their experiments to one million reversals of stress, yet some of the results are of considerable interest. The most striking fact which emerges is that while surface compression raises the endurance stress range, when the test piece is tested in air, to an appreciable extent (in some cases as much as 30 per cent.), the effect under exposure to water is still more marked. In at least two cases (nickel-steel and CrNiW steel) the endurance of the previously surface-compressed test piece when exposed to water was appreciably higher than that of the untreated test piece in air, the increase being 30 per cent. in the first and 26 per cent. in the second steel named under torsion. Under a bending test the surface-compressed steels also showed an advantage when tested in water as compared with the untreated material, but the difference is not so large.

The authors discuss this effect of surface compression at some length and discard the idea that the increased endurance brought about by this treatment is due to internal compressive stresses generated in the surface layers of the material, which would, to some extent, balance the tensile stresses which appear to be the destructive element of the fatigue cycle. They take the view that the action of so-called corrosion-fatigue is mainly due to the fact that when minute fissures are formed on the surface water enters these, and when the cycle is reversed it cannot be squeezed out sufficiently quickly, so that a wedge action occurs. In support of this view, they made tensile tests on portions of fatigue test pieces broken in air and in water respectively, and show that while in the former there were no indications of crack formation away from the main fracture, in the latter a multitude of minute surface cracks were opened up by tension. These, it is claimed, are more or less absent when the surface has been previously compressed.

The authors also record the observation that the commencement of corrosion, particularly in nickel-steel, occurs by the formation of small star-shaped accretions or corrosion products below which they find cracks showing corrosion damage. This they appear to regard as an original observation, although something very similar has been described and figured in the work of McAdam. It is, in fact, a striking and deplorable fact that these German authors did not think it necessary to refer to any of the work on corrosion-fatigue which has been done in America by McAdam and in this country by Gough, and prefer to discuss the few and more limited results which they themselves have obtained as a basis for theorising without availing themselves of the vast amount of material which has been collected by the authors named in years of patient research.

The Notched-Bar Impact Test.

FOR some years after its first introduction the notched-bar impact test was the subject of much controversy. There were some metallurgists who endeavoured to dispute its value entirely and who suggested that the phenomena of "notch brittleness" which it reveals have little or no bearing on the behaviour of materials in practice. Even as lately as the Zürich Congress in 1931 of the International Association for Testing Materials, an eminent British engineer boldly stated that he did not think that the notched bar impact test had any practical significance. Such an attitude towards it, however, must now be regarded as exceptional, since the test is widely used in varying forms throughout all engineering countries, and its value as a test of the quality

of a given material is fully recognised. Unfortunately, test pieces of different types have been developed in different countries, and it does not seem possible to find any formula by which results obtained from one type of test piece can be translated so as to correspond with those obtained from a different type. Efforts at international standardisation for such test pieces are being made, but owing to the great accumulation of data relative to any particular type of test piece for each country, such standardisation is bound to meet with serious difficulty.

Meanwhile, however, although there can be little doubt of the real value of the test, the question of what it is that it really determines requires much closer consideration. The test is generally spoken of as an " impact test " or " shock test," and yet the actual rate at which stress is applied to the test piece appears to make very little difference. Results show that it is a notched bar test rather than an impact test. Even then, however, it is not easy to specify precisely what are the qualities which it determines. The figures obtained in the test either in kilogramme-metres or foot-pounds are regarded as representing the energy absorbed in fracture, and this is related in some way to what may be roughly termed the " toughness " of the material. If it were possible in any material to cause fracture by separation along a single surface running between adjacent pairs of atoms, and to do this without disturbing the atoms in the subjacent layers on either side, extremely little work would be absorbed in the rupture. In practice this is never possible, and in the great majority of materials which are more or less ductile, deformation—that is, displacement of atoms or groups of atoms—occurs to a considerable depth on either side of the actual rupture, and it is the work done in producing this deformation which is mainly recorded by the notched bar impact test. It is, however, quite another matter to speak of this value as if it represented true resistance to rupture under shock or otherwise. Such a resistance must be measured not in work done when rupture has been completed, but in the amount of energy which has to be applied to a given piece of metal in order to produce rupture at all. This is a matter of the application of stress rather than of work done, but again the difficulty arises that in all ordinary methods of applying stress, deformation of a considerable volume of the metal occurs, and the phenomenon can scarcely be brought down to that of simple rupture on a single surface. Some approach to this type of test can be made by using a tensile test with notches of increasing sharpness and depth, and exterpolating from such a test for notches of infinite sharpness, and leaving only a very tiny portion of the test piece intact.

This type of notched bar tensile test is, however, unsatisfactory from two points of view. In the first place, it requires the use of a special type of test piece and the making of a series of tests with rather delicate machining of notches in each case. These facts alone would confine its use to research purposes. But beyond this comes the question how far, in such deeply and sharply notched test pieces, the rate of application of stress has an influence upon the result. Very little information on this point appears to be available, but it is a matter of some interest, and it would not be difficult for some of our engineering research laboratories to investigate the point. If it were found that " shock," due to the very rapid increase of stress in such a test, made a considerable difference to the result, then we should have a means of discriminating between materials which are sensitive to shock and those which are not. It might be possible to find in this way also some degree of correlation between results of a test of this kind and the well-known phenomena of notch sensitiveness in regard to fatigue testing. It is an interesting sidelight upon the view point which has been developed here that the notched bar impact figure shows no kind of correlation with notch sensitiveness under fatigue. Such correlation would not have been anticipated on the basis of the ideas outlined above.

The Alleged Allotropy of Aluminium.

Metallwirtschaft for November 17th last is remarkable because it contains two papers dealing with the above subject which come to entirely opposite conclusions. They have been purposely juxtaposed in order that a direct comparison of the views and evidence can be made, and this comparison is interesting.

In the first paper by A. Schulze evidence is given against the existence of an allotropic transformation in aluminium. This consists in showing in great detail that there are no discontinuities in a number of temperature-property curves. These are observed with sufficient accuracy on aluminium of the highest purity. This applies particularly to the change of electrical resistance with temperature which is regarded as one of the most sensitive tests for the existence of transformations, and curves both by the author and by Guertler and Anastasiadis are quoted. In every case it is shown that slight breaks in these curves occur when certain impurities, notably silicon and iron, are present in minute amounts, but that they disappear or tend to disappear in aluminium of increasing purity. Some heating and cooling curves by the two last-named authors are also given, but these, unfortunately, are small curves taken with the Saladin differential apparatus. Much stronger negative evidence of this kind has been obtained in England using apparatus of very much greater sensitivity. In fact, as long ago as 1912, Rosenhain and Archbutt showed, in connection with their study of alloys of aluminium and zinc, that the minute arrest points found in the best aluminium then available was in reality due to iron, since it lay on a continuous curve of arrest points found in alloys with increasing iron content.

Dilatometric evidence is also quoted, particularly the beautiful autographic curves obtained by Haas with his modification of the Chevenard dilatometer.

Finally, and we cannot help thinking conclusively, the matter is settled by X-ray analysis of aluminium at high temperatures which has been undertaken by Alichanow, who found that there was no change of lattice structure, except that which could be accounted for by normal thermal expansion.

In spite of this mass of negative evidence against the existence of any transformation in aluminium, O. Tiedemann maintains that a transformation point does exist in aluminium, and that the absence of breaks in any number of temperature-property curves cannot be regarded as conclusive proof that there is no transformation. He seeks to support this by comparison with other metals, but one cannot help thinking that his choice of these comparisons is not only unfortunate but definitely biased. It is, we

think, generally admitted to-day that the magnetic transformation of iron at the A 2 point is not an allotropic change, since it is not accompanied by any change of crystal lattice. All this example serves to prove is that one may obtain breaks in temperature-property curves, and even a marked evolution or absorption of heat, where there is no real allotropic transformation. It can scarcely serve to prove the contrary. On the other hand, the well-known and marked transformation of iron at A 3 is ignored by Tiedemann who prefers to discuss the very doubtful question of the supposed transformations in zinc. There, also, X-ray analysis has shown the absence of a lattice change, so that, again, Tiedemann is discussing a case in which real transformations have not been established. He also suggests that with silver and copper there are reasons to suppose the existence of transformations which do not reveal themselves by irregularities in electrical conductivity or other temperature-property curves.

Reading the two papers together, one can hardly fail to arrive at the conclusion that evidence against the existence of an allotropic transformation in aluminium is too strong to be upset by the kind of argument introduced by Tiedemann, and this conclusion, drawn from the work of the German investigators, will serve to confirm the view which has for a long time been held by those engaged upon researches in connection with aluminium in this country.

Books and Publications.

A Text-book of Fire Assaying. By EDWARD E. BUGBEE. Second edition. New York: John Wiley and Sons. London: Chapman and Hall.

THIS volume is a revised and enlarged edition of a work which was published by the Associate Professor of Mining Engineering and Metallurgy at the Massachusetts Institute of Technology in 1915.

In scope it follows that of earlier contributions to the literature of this branch of metallurgy made from time to time by members of the staffs of the Schools of Mines in the United States. Such works as those of Ricketts and Miller, Lodge, Fulton, and Furman have provided many generations of students with useful guides to American practice, while British students have relied largely upon the text-books of J. J. Beringer, Ernest A. Smith, E. A. Wraight, and others, over the same period.

The present volume exhibits evidence of a careful consideration of the available literature, and includes much information which has not hitherto been readily accessible to the general student. The author has studiously avoided what he refers to as the "cook-book" method of presentation, and has endeavoured to give the scientific reasons underlying many of the phenomena which are met with in this branch of metallurgy. He believes that, if approached in a proper way, a course in fire-assaying is "the logical place to introduce the study of metallurgy," and that general metallurgy is "made concrete and intensely interesting if the various processes of fire-assaying are used to illustrate its principles."

After preliminary chapters on Reagents and Equipment, the author proceeds to deal with the all-important matter of sampling.

The chapter on the "Scorification Assay" raises the question of the continued use of this procedure, which involves operations on comparatively small samples where the representative character of such samples must be beyond doubt. The author is careful, however, to point out the limitations of this method, and to give warnings in regard to cases in which its use is not to be recommended (pages 134 and 138). He also indicates (page 223) directions in which this method, hitherto in general use, has now fallen into disfavour, being replaced by the crucible method.

The chapter on the "Crucible Assay" is perhaps the most important, and considerable space has been devoted to it. The various factors which enter into the operations of making satisfactory assays by this method are given due consideration. Types of ores which may be met with are classified according to their oxidising or reducing character, and the functions of the more important fluxes are discussed.

A useful chapter follows on the assay of complex ores and the use of special methods.

The chapter on the Assay of Bullion conforms generally with the accounts given in other standard works. Here, again, prominence is given to the question of sampling. The paragraph "Sampling Molten Bullion," however, calls for some comment and a warning. The author says that the most satisfactory method is to melt the whole and stir thoroughly with a graphite rod or iron bar, and then to ladle out a small amount and granulate it by pouring into water. The use of iron, either in stirring or in sampling molten gold bullion, is only to be adopted with the greatest care and with a full knowledge of the possible consequences. The solubility of iron in gold is such that there is a grave risk of contaminating both the sample and the bullion itself. It is true that iron ladles are used for this purpose, but only when thickly coated with a graphitic mixture, and the operation is performed so quickly that any danger of contact with the iron is averted. Nevertheless, the use of graphite or "salamander" stirrers and ladles is preferable.

Short chapters are given on the Assay of Solutions and on the Lead Assay, and the volume concludes with an account of methods for the assay of ores and products containing metals of the platinum group.

The ancient art of fire-assaying, which has been practised for generations by skilled craftsmen who have brought to their work much careful observation and experience, has now the added advantage of the services of those who, with a broader general scientific training, are able, not only to appreciate the merits of empirical procedures of long standing, but are also able to introduce modifications in practice where improvements are desirable and where such modifications can be shown to lead to improvements.

As an accompaniment to an organised laboratory course of "fire-assaying," and to those who have already profited by such a course, this volume may be safely commended.